



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

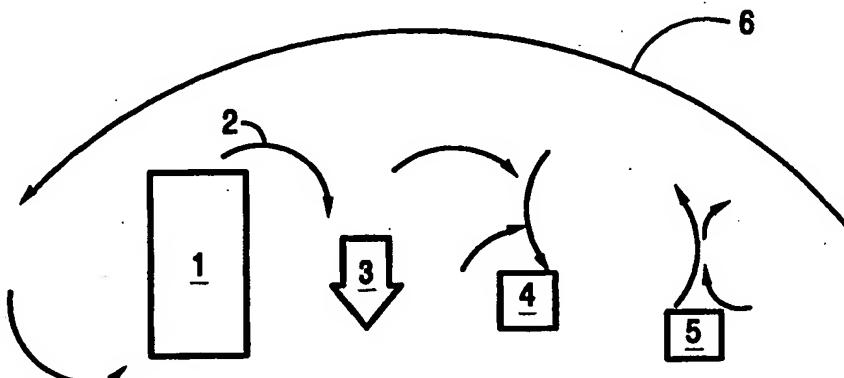
(51) International Patent Classification 6 : <b>B01D 53/50, 53/56, 53/75, 53/96, C01B 17/74</b>		A1	(11) International Publication Number: <b>WO 99/26714</b>
			(43) International Publication Date: 3 June 1999 (03.06.99)

(21) International Application Number: <b>PCT/US98/23669</b>	(81) Designated States: AU, CA, JP, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 6 November 1998 (06.11.98)	
(30) Priority Data: 08/978,249 25 November 1997 (25.11.97) US	Published <i>With international search report.</i>
(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).	
(72) Inventors: JOHNSON, David, Lee; 181 Concord Meeting Road, Glen Mills, PA 19342 (US). NARIMAN, Khushrav, Erach; 13411 Melville Lane, Chantilly, VA 20151 (US). STERN, David, Lawrence; 3906 Tambrook Drive, Mount Laurel, NJ 08054 (US).	
(74) Agents: PRATER, Penny, L. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).	

(54) Title: PROCESS FOR THE REDUCTION OF SO<sub>2</sub> FROM WET LIME/LIMESTONE TAILGAS IN POWER PLANT DESULFURIZATION PROCESSES

(57) Abstract

This invention describes a process for the scrubbing of sulfur oxides (2) from the effluent of conventional wet lime/limestone sulfur oxides reduction processes (3) in coal or oil fired plants (1). The sulfur oxides are oxidatively sorbed onto solid sorbents (4) such as magnesium aluminate spinel. Reduction with the appropriate reducing gases (such as hydrogen) regenerates the solid sorbent (5), which also yields a process stream containing sulfur oxides. The sulfur oxides containing stream (6) can be re-fed to the front end of the coal or oil fired plants (1), with the sulfur oxides thus produced ultimately being removed in the conventional wet scrubbing technology (3). This process may allow for the use of high sulfur fuels.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	MW	Malawi	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

PROCESS FOR THE REDUCTION OF SO<sub>2</sub>  
FROM WET LIME/LIMESTONE TAILGAS IN POWER PLANT  
DESULFURIZATION PROCESSES

5

This invention describes a process for the scrubbing of sulfur oxides, using a solid sorbent such as a magnesium aluminate spinel, from the effluent of conventional wet lime/limestone SOx reduction processes in coal or oil-fired plants.

10 In the Claus process, elemental sulfur is produced by reacting H<sub>2</sub>S and SO<sub>2</sub> in the presence of a catalyst. The Claus system uses a combustion chamber which, at 950° to 1350°C, converts 50 to 70% of sulfur contained in the feed gas into elemental sulfur. Sulfur is condensed by cooling the reaction gas to a temperature below the dew point of sulfur, after which the remaining gas is heated and further reacted over a catalyst. Normally, the gas passes through at least two such Claus catalyst stages.

15 The use of magnesium aluminate spinels for the oxidative sorption of SOx from effluent streams of the Claus process, followed by the reductive regeneration and reprocessing of the off-gas thus produced, has received recent attention as an attractive means to limit the potential for environmental damage which may be caused from the direct release of SOx.

20 The Mobil Oil SOx Treatment Process (MOST) is currently under development for a number of different applications. The first envisioned use of this technology, for Claus Tailgas scrubbing, was disclosed in U.S. Patent No. 5,229,091. It consists of the oxidative sorption of SO<sub>2</sub> onto a solid sorbent, preferably a magnesium aluminate spinel, followed by reductive regeneration to produce an effluent containing primarily SO<sub>2</sub>, with some H<sub>2</sub>S and S. This effluent is then re-fed to the Claus Unit for further reaction. The sulfur oxide sorbed is 25 ultimately transformed into elemental sulfur. Reductive desorbents (reducing gases) found to be successful for this are hydrogen, hydrocarbons (methane, propane), carbon monoxide/synthesis gas combinations, hydrogen sulfide, and ammonia.

30 In addition to the aforementioned Claus Tailgas scrubbing application, other modes of implementing this scheme have been put forth and investigated. Some of those modes involve the scrubbing of FCC tailgas in a manner similar to that described for Claus Tailgas operations. U.S. Patent No. 5,547,648 discloses this concept. The MOST process has also been extended to gas field applications, process heat furnaces, and to coal or oil fired plants. The process for the oxidative sorption of SOx is similar in the applications listed here. The 35 availability of reducing gases and related process equipment allows for a fairly wide number of applications for this technology.

35 The use of technology for the scrubbing of SOx via sorption onto solid sorbents such as metal oxides (i.e., MOST), from the tail end of conventional technology in power plant applications is disclosed in this invention. Conventional technology, such as wet lime/limestone slurries, allows for the removal of up to 90% of sulfur oxides. MOST technology can 40 capture >99.9% of the SOx in process streams, as previous patents, such as those disclosed

in the background indicate. Thus, a MOST-type process could significantly lower the SO<sub>x</sub> emissions from conventional scrubber operations and allow for the use of higher sulfur-content fuels in power plant operations.

This application discloses a process for the scrubbing of sulfur oxides from the effluent of conventional wet lime/limestone SO<sub>x</sub> reduction processes in coal or oil-fired plants. The sulfur oxides are oxidatively sorbed onto magnesium aluminate spinel as solid sorbent. Reduction with the appropriate reducing gases (such as hydrogen) regenerates the catalyst, also yielding a process stream concentrated in SO<sub>x</sub>. This concentrated SO<sub>x</sub> stream can then be re-fed to the front end of the coal or oil-fired plants, with the SO<sub>x</sub> thus produced ultimately being removed in the conventional wet scrubbing technology. This process is capable of capturing >99% of the SO<sub>x</sub> from power plants, a significant advantage over commercial wet lime/ limestone processes alone, where only 90% of the SO<sub>x</sub> can be removed, and may allow for the use of high sulfur fuels (having a sulfur content of 4% or greater) in power plant applications.

The concept of utilizing the Claus reaction for the conversion of SO<sub>2</sub> to elemental sulfur in power plant applications is known. To the best of our knowledge, however, this is the first example of technology whereby sulfur oxides can be reduced to very low levels following conventional power plant scrubbing technology.

Regulatory requirements have and will continue to force reductions in sulfur oxide emissions from various sources. Solid, regenerable SO<sub>x</sub> sorbents show promise for controlling these acid rain precursors by scrubbing these environmental contaminants prior to their release in the atmosphere.

The Figure illustrates the process steps of the instant invention.

The process described may be thought of as follows (see Figure): A fuel such as coal or oil is burned in the burner (1) to provide the energy input necessary ultimately for power generation. Approximately 90% of the SO<sub>x</sub> thus produced is then removed (2) via conventional wet lime/limestone scrubbing technology (3) such as that disclosed in U.S. Patent No. 5,298,473. Following limestone scrubbing, the residual SO<sub>x</sub> in the effluent (tailgas) from this wet scrubbing process is oxidatively sorbed onto a solid sorbent located within an absorber (4), preferably a magnesium aluminate spinel as described in U.S. Patent No. 5,229,091 (Buchanan et al.). The sulfated sorbent in the absorber is then reduced (5) to regenerate the sorbent and to desorb primarily sulfur oxides. Reductants for this process could include hydrogen, CO, C<sup>1</sup> to C<sup>5</sup> hydrocarbons, H<sub>2</sub>S, and other reducing gases. Hydrogen is preferred, however. The offgas is then re-fed to the burner (6) where all sulfur species are converted to SO<sub>2</sub>. The conventional wet scrubbing process will ultimately remove the sulfur oxides, which are recycled to extinction. The use of a sorbent system (i.e., MOST) in which >99.9% of the SO<sub>x</sub> can be removed, is key in further reducing sulfur oxide emissions from a power plant facility.

The solid sorbents can be impregnated or otherwise coated with an oxidizing catalyst or promoter that promotes the removal of nitrogen oxides and the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the presence of oxygen. It is believed that  $\text{SO}_3$  is more readily adsorbed than  $\text{SO}_2$ .

One useful catalyst is ceria (cerium oxide). Another useful catalyst is platinum. Other

5 catalytic metals, both free and in a combined form, preferably as an oxide form, can be used, either alone or in combination with each other or in combination with ceria and/or alumina, such as rare earth metals, metals from Group 8 of the Periodic Table, chromium, vanadium, rhenium, tungsten, silver, and combinations thereof. The sulfur oxide-capturing absorbent can be in the form of balls, pebbles, spheres, extrudates, channeled monoliths, microspheres or  
10 pellets.

It is preferred to operate the absorber containing the solid sorbent at a temperature from 482° to 760°C (900° to 1400°F). A temperature of from 593° to 704°C (1100° to 1300°F) is most preferred. Oxygen should be introduced into absorber in an amount of from 0.10 to 10 vol.%. Two to 4 vol.% is preferred, however. Pressure within the absorber should be

15 maintained at a pressure of from 500 to 20,000 GHSV. Three thousand to 5,000 GHSV is preferred. An additional benefit of operating the absorber within these parameters is that any carbon monoxide therein is converted into carbon dioxide which is released into the environment. Other gases released from the absorber include nitrogen, oxygen, and trace amounts of sulfur dioxide along with water.

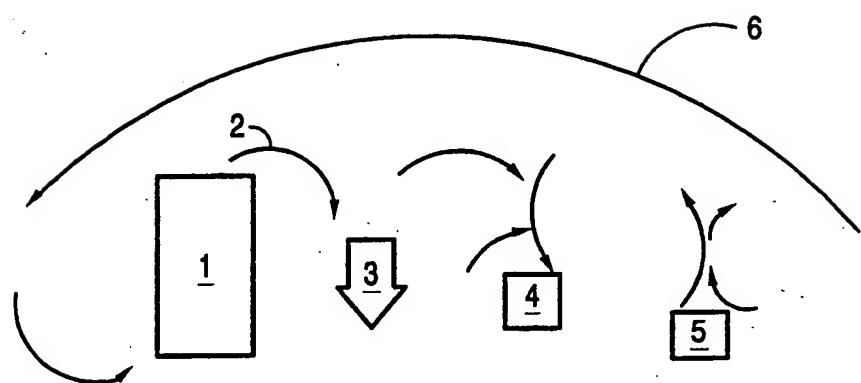
20 The operating parameters for the regeneration of the sorbent are equally applicable to both fluidized and fixed bed processes. Initially a GHSV of 300 should be used when commencing regeneration of the fixed bed absorbent so that a higher concentration of liberated gases can be removed from the regenerator. As regeneration proceeds, the GHSV can be reduced to 50 as the concentration of liberated gases diminishes. Substantially  
25 improved regeneration results are anticipated when water is co-fed into the regenerator along with the hydrocarbons. Once regeneration is completed, liberated sulfur dioxide, hydrogen sulfide, and water are recycled to the burner.

The MOST process, including operating conditions and conditions for regeneration of the sorbent, is more fully described in U.S. Patent No. 5,229,091.

CLAIMS:

1. A process for the elimination of nearly all sulfur oxide emissions from a power plant facility, the facility comprising a burner, a wet lime/limestone scrubber, and an absorber which further comprises a solid sorbent, the process comprising the following steps:
  - 5 (a) burning a fuel in the burner to provide the energy input necessary for power generation, thereby producing sulfur oxide emissions in the tailgases of the burning process;
  - (b) removing 90% of the sulfur oxide emissions of step (a) via treatment of the tailgases with a wet lime or limestone scrubber;
  - 10 (c) removal of sulfur oxides not removed in step (b) by sorbing in the presence of oxygen onto a solid sorbent, until the sorbent is saturated;
  - (d) treating the saturated solid sorbent with reducing gases in order to regenerate the solid sorbent and to desorb sulfur oxides in the offgas; and
  - (e) re-feeding the offgas to the burner of step (a), where sulfur oxides are converted to  $\text{SO}_2$ .
2. The process of claim 1, wherein the reducing gases of step (d) are selected from the group consisting of hydrogen, carbon monoxide, hydrogen sulfide, and  $\text{C}^1$  to  $\text{C}^5$  hydrocarbons.
3. The process of claim 1, wherein the solid sorbent comprises a spinel.
- 20 4. The process of claim 3, wherein the spinel is a magnesium aluminate spinel.
5. The process of claim 1, wherein over 99.9% of the sulfur oxides can be removed from the tailgas effluent.
6. The process of claim 1, wherein the solid sorbent is selected from the group consisting of balls, pebbles, spheres, extrudates, channeled monoliths, microspheres or pellets.
- 25 7. The process of claim 1, wherein the solid sorbent is impregnated or otherwise coated with an oxidizing catalyst or promoter that promotes the removal of nitrogen oxides and the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the presence of oxygen.
8. The process of claim 7, wherein the oxidizing catalyst or promoter comprises ceria or Pt.
- 30 9. The process of claim 1, wherein the absorber comprising the solid sorbent is operated at a temperature from 402° to 760°C (900° to 1400°F).
10. The process of claim 1, wherein oxygen is introduced into the absorber in an amount of from 0.10 to 10 vol.%.

1/1

*FIGURE*

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/23669

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01D 53/50, 53/56, 53/75, 53/96; C01B 17/74  
US CL :423/239.1, 242.1, 243.08, 244.01, 244.10, 533, 536

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/239.1, 242.1, 243.08, 244.01, 244.10, 533, 536, 555

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,547,648 A (BUCHANAN et al) 20 August 1996, please see col. 5 lines 54-55; col. 6 lines 5-47; col. 7 lines 19-21 and lines 34-36; col. 15 line 45 to col. col. 16 line 23 and col. 21 lines 37-52.	1-10
Y	US 4,183,908 A (ROLFE) 15 January 1980, please see col. 1 lines 5-30.	1
A,P	US 5,728,358 A (AVIDAN et al) 17 March 1998, please see col. 1 line 65 to col. col. 5 line 15.	1-10
A	US 5,283,055 A (LUCK) 01 February 1994, please see col. 2 lines 4-21.	1-10
A	US 5,229,091 A (BUCHANAN et al) 20 July 1993, please see col. 3 lines 27 to col. 34.	1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A"	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

07 JANUARY 1999

Date of mailing of the international search report

16 FEB 1999

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer  
S. Handley  
TIMOTHY C. VANOV

Telephone No. (703) 308-0661

**INTERNATIONAL SEARCH REPORT**

International application No. PCT/US98/23669
---

**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95/03876 A (CORMA CANOS et al) 09 February 1995, please see the English abstract.	1-10